

Quantifying Polarization losses at liquid electrolyte / single ion conductor (SIC) interface

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Single Ion conductor solid electrolytes such as OHARA® glass ($\text{Li}_{1+x+3z}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_{3z}\text{P}_{3-z}\text{O}_{12}$) are being considered for protection from dendrites in Li metal-based batteries such as Li-S and Li-air. OHARA® glass is a single ion conductor (SIC) with a Li ion transference number of unity. Previous studies¹ using AC Impedance spectroscopy has shown that a high-energy barrier exists at the SIC/liquid electrolyte interface. Such a charge transfer resistance has been attributed to desolvation of the Li ion. To further investigate this phenomenon, a custom diffusion cell was designed where the SIC was sandwiched between two independent compartments in a Li-Li symmetric cell (Figure 1). LiPF_6 in EC:DEC (1:1) was used as the electrolyte in the study,. Constant current experiments were performed with and without the SIC in the cell to quantify the polarization loss at the SIC/liquid electrolyte interface. A mathematical model was developed to estimate the potential drop in the system, as described below.

When a constant current is passed through a Li-Li symmetric cell, flux equal to current boundary condition is maintained at the two electrodes. When a constant current is passed through the Li-Li symmetric cell with a single-ion conductor (SIC) sandwich, only Li ions pass through from one compartment to the other. In order to maintain electro-neutrality, the flux of Li ions at the SIC/liquid electrolyte interface has to be equal to the current being maintained in the cell. As a consequence, in a Li-Li symmetric cell of length 'L' with a SIC in the middle, the concentration profiles of Li ions in each compartment would be that of a Li-Li symmetric cell of length 'L/2'. Therefore, in principle, if there are no interfacial effects at the SIC/liquid electrolyte interface and current is passed for a short period of time (semi-infinite boundary condition maintained), then the overall cell potential should be the sum of: (a) potential drop in a Li-Li symmetric cell without the SIC; (b) Ohmic drop through the SIC; (c) concentration over potential right next to either sides of the SIC/liquid electrolyte interface.

Figure 2 shows experimental results for 0.5M electrolyte concentration where the cell potential was measured at different current densities in a Li-Li symmetric cell with SIC (purple dots) and without SIC (red dots). The solid red line shows the model predictions without interfacial effects. Clearly the polarization loss for the case with SIC was much higher than what was expected from theory indicating that the interfacial effects are significant.

Overall, this talk will show:

- (a) The methodology to quantify polarization losses at SIC / liquid electrolyte interface
- (a) That the polarization losses at SIC / liquid electrolyte interface are significant
- (b) That the interfacial effects are concentration dependent
- and
- (c) That the polarization losses are dynamic in nature

Such polarization losses can limit the maximum current densities that can be operated in such cells and understanding their nature is paramount for future battery development.

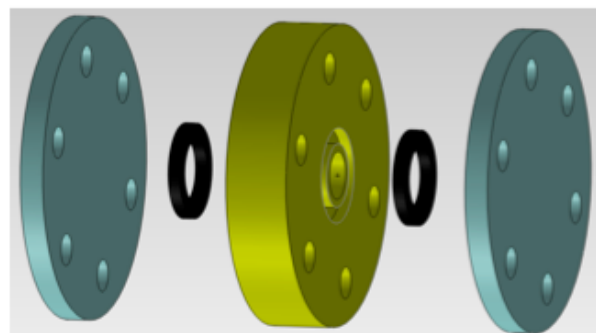


Figure 1. Schematic of custom Li-Li symmetric diffusion cell

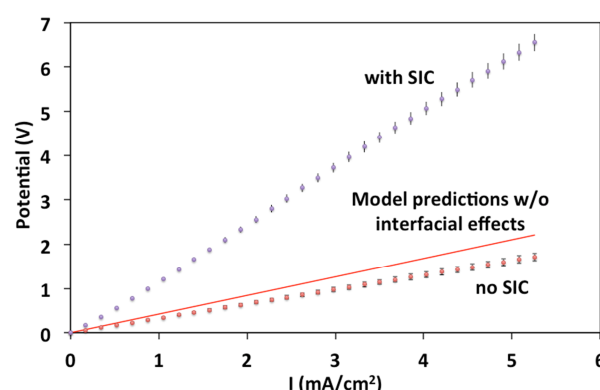


Figure 2. Cell potential at different current densities in the Li-Li symmetric cell with and without SIC in the middle for 0.5M LiPF_6 in EC:DEC (1:1) electrolyte.

References

1. T. Abe, F. Sagane, M. Ohtsuka, Y. Iriyama, Z. Ogumi, J. Electrochem. Soc, 152, (111) A2151, (2005).